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(54) Olefin polymer adhesive
compositions

(57) Adhesive blends that are strong adhesives to various substrates and especially to polar substrates, comprise (a) a graft copolymer of a polyethylene backbone grafted with at least one grafting monomer which is a polymerizable ethylenically unsaturated carboxylic acid or derivative thereof, (b) a LDPE, a linear low density polyethylene, or an ethylene-unsaturated ester copolymer and (c) a homo- or copolymer of an α -olefin having 4 to 15 carbon atoms.

GB 2 113 696 A

SPECIFICATION

Polyethylen graft copolymer - containing adhesive blends and composite structures made with them

5 The present invention is concerned with adhesive blends containing polyethylene graft copolymers and with their use in composite structures. 5

It is known that blends of high density polyethylene (HDPE), low density polyethylene (LDPE), or ethylene-vinyl acetate copolymers (EVA) with polyethylene graft copolymers in which polyethylene is grafted with suitable unsaturated carboxylic acids or carboxylic acid anhydrides or other acid derivatives, are 10 adherent to certain polar polymers, such as polyamides. On the other hand, the adhesion of such blends to certain other polar polymers, such as polyesters and saponified ethylene-vinyl acetate copolymers (ethylenevinyl alcohol copolymers [EVOH]), is insufficient in many cases. 10

We have now found that by adding polymers of α -olefins having 4 to 15 carbon atoms to such blends, adhesive blends are obtained which provide high bond strength to polyesters and ethylene-vinyl alcohol 15 polymers, while also providing excellent bond strength to polyolefins and polar substrates, such as other kinds of polar polymers, for example polyamides, metals, glass, paper, wood and leather. 15

According to the present invention, therefore, there is provided an adhesive blend which comprises, by weight:

(a) from 0.1 to 40 parts of a graft copolymer of from 70 to 99.999% of a polyethylene backbone grafted 20 with from 30 to 0.001% of at least one grafting monomer which is a polymerizable ethylenically unsaturated carboxylic acid or derivative thereof, for a total of 100%, 20

(b) from 0.1 to 99 parts of LDPE, an ethylene-unsaturated ester copolymer, or LLDPE, or a mixture of two or more thereof, and

(c) from 0.1 to 99 parts of at least one homopolymer or copolymer of an α -olefin having 4 to 15 carbon 25 atoms, for a total of 100 parts. 25

The backbone of the graft copolymer forming component (a) of the adhesive blend according to the invention may be an ethylene homopolymer or a copolymer of ethylene with one or more higher alkenes, such as propylene, butene-1, hexene-1, 4-methyl-pentene-1, or octene-1, and may further contain di- or tri-olefins as are used commercially in ethylene-propylene terpolymers, such as ethylidene-norbornene, 30 methylene-norbornene, 1,4-hexadiene, and vinylnorbornene. Where an ethylene copolymer is used, the comonomer(s) is/are preferably present in an amount up to 40% by weight. Mixtures of two or more such homo- or co-polymers may also be used as the backbone polymer. Linear polyethylenes which are of high, medium or low density, are preferably used as the backbone polymer. 30

Suitable unsaturated carboxylic acids and derivatives thereof for use as the grafting monomer include, for 35 example, acrylic acid, methacrylic acid, fumaric acid, maleic acid, maleic anhydride, 4-methyl cyclohex-4-ene-1,2-dicarboxylic acid anhydride, bicyclo (2.2.2)oct-5-ene-2,3-dicarboxylic acid anhydride, 1,2,3,4,5,8,9,10-octahydronaphthalene-2,3-dicarboxylic acid anhydride, 2-oxa-1,3-diketospiro(4.4)non-7-ene, bicyclo (2.2.1)hept-5-ene-2,3-dicarboxylic acid anhydride, maleopimaric acid, tetrahydrophthalic anhydride, x-methylbicyclo(2.2.1)hept-5-ene-2,3-dicarboxylic acid anhydride, x-methylnorborn-5-ene-2,3-dicarboxylic 40 acid anhydride, norborn-5-ene-2,3-dicarboxylic acid anhydride, Nadic anhydride, methyl Nadic anhydride, Himic anhydride, methyl Himic anhydride and other fused ring monomers described in U.S. Patents 3,873,643 and 3,882,194. 40

Of these maleic anhydride, fumaric acid, x-methylbicyclo(2.2.1)hept-5-ene-2,3-dicarboxylic acid anhydride and bicyclo(2.2.1)hept-5-ene-2,3-dicarboxylic acid anhydride are particularly preferred.

45 Cograftering monomers as described in U.S. Patent 3,882,194 may also be used in preparing the graft copolymer. Among the conjugated unsaturated esters suitable for such cograftering are, for example, dialkyl maleates, dialkyl fumarates, dialkyl itaconates, dialkyl mesaconates, dialkyl citraconates, alkyl acrylates, alkyl crotonates, alkyl tiglates and alkyl methacrylates where alkyl is an aliphatic, aryl-aliphatic or cycloaliphatic group containing 1-12 carbon atoms. Preferred esters for use as cograftering monomers are 50 dibutyl maleate, diethyl fumarate and dimethyl itaconate. 50

The graft copolymer is, in general, made by heating a mixture of the backbone polymer or polymers and the grafting monomer or monomers with or without a solvent and with or without a catalyst. Heating may be effected to a temperature above the melting point of the polyolefin. Thus, grafting may be effected in the presence of air, a hydroperoxide or other free radical catalyst or preferably in the essential absence of those 55 materials where the mixture is maintained at elevated temperatures and (if no solvent is used) preferably under high shear. 55

A convenient method of carrying out the reaction is to premix the ingredients and then extrude the composition through a heated extruder. Other mixing means, such as a Brabender mixer, a Banbury mixer, or a roll mill, can also be used. In order to prevent undue increase in molecular weight with a possibility of 60 some cross-linking at elevated temperatures, it is preferred to carry out the reaction in a closed vessel. A conventional single or multiple screw extruder accomplishes this result without the use of auxiliary equipment and for this reason is a preferred apparatus for carrying out the grafting reaction. 60

The graft and cografter copolymers are recovered by any method or system which separates or utilizes the graft copolymer that is produced. Thus, the copolymer may be recovered, for example, in the form of 65 precipitated fluff, pellets, or powders, or as further chemically reacted or blended pellets or powders, or in 65

the form of shaped articles formed directly from the resulting copolymer.

When the graft copolymer comprises solely the backbone polymer and a grafting monomer which is an ethylenically unsaturated carboxylic acid or derivative thereof, it preferably comprises 70 to 99.95% by weight of the backbone polymer and 30 to 0.05% by weight of the grafting monomer. Graft copolymers, which additionally comprise an unsaturated ester as graft monomer, preferably comprise 50 to 99.9% by weight of the backbone polymer, 0.05 to 25% by weight of the unsaturated acid or acid derivative, and 0.05 to 25% by weight of the unsaturated ester.

Component (b) of the adhesive blend according to the invention is a linear low density polyethylene (LLDPE) which is generally prepared by polymerization in the presence of a transition metal catalyst, such a compound of titanium, vanadium, aluminium, chromium, or the like, or a branched low density polyethylene (LDPE) prepared by high pressure polymerization, or a copolymer of ethylene and an unsaturated ester, such as vinyl acetate, ethyl or methyl acrylate, or ethyl or methyl methacrylate. The density of this component is preferably from 0.91 to 0.97 g/cc and its MI is preferably 0.1 to 100g/10 min. The preferred material for component (b) is polyethylene having a density of 0.91 to 0.93 g/cc and a MI of 0.5 to 20g/10 min.

Component (c) of the adhesive blend according to the invention is a homopolymer or copolymer of an α -olefin having 4 to 15 carbon atoms, such as butene-1, 4-methyl-pentene-1, hexene-1, octene-1, and pentene-1. In the case of copolymers, the copolymer should contain at least 50% by weight of such an α -olefin. The preferred poly- α -olefin is poly(butene-1) having a density of 0.88 to 0.93 g/cc and a MI of 0.5 to 50g/10 min as determined by ASTM Test Procedure D1238.

The adhesive blend according to the invention preferably also contains one or more antioxidants appropriate to the constituents thereof.

The present invention also comprises a composite structure comprising a substrate and, adhered thereto, an adhesive blend according to the invention, and further comprises a composite structure comprising two or more substrates with adjacent pairs of substrates adhered together by an interposed layer of an adhesive blend according to the invention.

These composite structures may comprise polar substrates, such as nylon, ethylene-vinyl alcohol copolymers (EVOH), poly-vinyl alcohol (PVA), polyester, polyurethane, metals, glass, wood, paper, leather, and regenerated cellulose. Such substrates may be adhered to substrates formed of polyolefins, such as polyethylene (PE), ethylene vinyl-acetate copolymers (EVA) or ethylene copolymers with other monomers, and polypropylene (PP). Other combinations can readily be made by those skilled in the art.

Such composite structures can be made by lamination, coextrusion, extrusion lamination, coextrusion coating of any other method for joining dissimilar materials to form composite structures known to those skilled in the art.

Some examples of these composites are: adhesive of this invention/nylon, adhesive/polyethylene, adhesive/polyester, adhesive/ethylene-vinyl acetate copolymer, adhesive/ethylene-vinyl alcohol copolymer, adhesive/aluminium, adhesive/steel, adhesive/glass, adhesive/wood, adhesive/leather, polyolefin/adhesive/nylon, polyolefin/adhesive/EVOH, adhesive/nylon/adhesive/polyolefin, polyolefin/adhesive/EVOH/adhesive/polyolefin, polyolefin/adhesive/polyester, EVA/adhesive/EVOH, EVA/adhesive/polyesters, polyolefin/adhesive/polyester/adhesive, and polyolefin/adhesive/polyester/adhesive/polyolefin.

Examples of other combinations are aluminium/adhesive/aluminium or adhesive/aluminium/adhesive or polyolefin/adhesive/aluminium/adhesive/polyolefin. Other metals, such as copper, steel or brass, can also be used. Dissimilar metal examples are: aluminium/adhesive/copper, aluminium/adhesive/steel, and aluminium/adhesive/brass. Composites of the type metal/adhesive/polar polymer can also be made, such as aluminium/adhesive/nylon, aluminium/adhesive/EVOH, or steel/adhesive/nylon/adhesive/steel. Here again, other combinations will readily occur to those skilled in the art.

Polyester substrates comprise both homopolymers (essentially comprising the reaction product of a dicarboxylic acid or derivative thereof with a diol or derivative thereof) and copolymers (essentially comprising the reaction product of one or more dicarboxylic acids or derivatives thereof with one or more diols or derivatives thereof). The dicarboxylic acids and the diols referred to may be aliphatic, aromatic or alicyclic. Examples of such carboxylic acids are terephthalic acid, isophthalic acid, and cyclo-hexane-dicarboxylic acid. Examples of such diols are ethylene glycol, dihydroxy-propene (propylene glycol), dihydroxybutene (butylene glycol), dihydromethylbenzene, and dihydromethylbenzene, and dihydromethylcyclohexane.

The composites of this invention can be used to manufacture a variety of useful articles. They can be used as packaging films, blow moulded bottles, co-extruded sheet which can be thermoformed into containers, coatings on glass bottles or wood or metal or even to join two metals, either the same metal or dissimilar metals, into a lamination.

In preparing the blends of this invention from the above graft copolymers, ethylene homopolymers and copolymers, and poly(α -olefin)s, any suitable blending equipment or technique may be used. In the Examples below, the blends were prepared in an electrically heated Brabender Plasticorder mixing head using a scroll type mixer under the following conditions: temperature - 325°F (163°C), rotor speed - 120 rpm, and mixing time - 10 minutes after flux.

In most of the specific examples, the resultant blends were compression moulded into films approximately 0.005-0.007 inch (0.13-0.18mm) thick. The films were then heat sealed to the substrate under evaluation at an appropriate temperature and time. The resultant composites were tested by cutting into

strips one inch (2.54 cm) wide and testing adhesion by a T-peel test similar to that described in ASTM D187-72.

In order that the invention may be more fully understood, the following examples are given by way of illustration only. All parts and percentages are by weight.

Example 1

An electrically heated C.W. Brabender mixing unit was used to blend 45% of a linear low density polyethylene resin having a melt index of 3.1 G/10 min. and a density of 0.921 g/cc with 45% of a poly(butene-1) having a melt index of 1.0 g/10 min. and a density of 0.910 g/cc, and 10% of a high density polyethylene of density 0.96 g/cc grafted with x-methyl bicyclo(2.2.1) hept-5-ene-2,3-dicarboxylic acid anhydride (XMNA) such that the grafted high density polyethylene had a melt index of 1.5 g/10 min. and graft level of 1.5%.

The blend was tested for adhesion to ethylene-vinyl alcohol copolymer film on a heat sealer set at 430°F (221°C) for 1 sec. An inseparable bond was obtained, the adhesion being greater than 6.6 lb/in (1.19 kg/cm).

Example 2

The poly(butene-1) of Example 1 was changed to one with a melt index of 1.8 g/10 min. and a density of 0.915 g/cc. The blend thus prepared gave an inseparable bond with adhesion greater than 6.9 lb/in (1.24 kg/cm) when heat sealed to a film of ethylene-vinyl alcohol copolymer at 430°F (221°C) for 1 sec.

Example 3

The poly(butene-1) of Example 1 was changed to one with a melt index of 2.0 g/10 min. and a density of 0.908 g/cc. The blend thus prepared when heat-sealed at 430°F (221°C) and 1 sec. to the following substrates and the following peel strengths were observed:

Substrate	Adhesion lb/in (kg/cm)	Bond
Ethylene-vinyl alcohol copolymer	>7.3 (1.31)	inseparable
Medium density poly- ethylene, MI 3, density 0.932	>7.5 (1.35)	inseparable
Nylon 6	3.9 (0.70)	elongation

Example 4

An electrically heated C.W. Brabender mixing unit was used to blend 45% of a medium density polyethylene of melt index 3 g/10 min. and density of 0.932 g/cc with 45% of a poly(butene-1) of melt index 2.0 g/10 min. and density 0.908 g/cc, and 10% of high density polyethylene grafted with x-methyl bicyclo(2.2.1)hept-5-ene-2,3-dicarboxylic acid anhydride similar to that used in Example 1.

This blend was then heat-sealed to nylon 6 and to ethylene-vinyl alcohol copolymer at 430°F (221°C) and 1 sec. The adhesion to nylon 6 was 2.6 lb/in (0.47 kg/cm) and 3.0 lb/in (0.54 kg/cm) to ethylene-vinyl alcohol copolymer.

Example 5

The linear low density resin of Example 3 was replaced by one with a melt index of 2.5 g/10 min. and a density of 0.918 g/cc. The blend thus made was heat-sealed to films of nylon 6 and ethylene-vinyl alcohol copolymer at 430°F (221°C) and 1 sec. The adhesion was greater than 5.4 and 7.1 lb/in (0.97 and 1.28 kg/cm) respectively. Inseparable bonds were obtained.

Examples 6-22

An electrically heated C.W. Brabender mixing unit was used to blend a linear low density polyethylene (LLDPE) resin of melt index 2.0 g/10 min. and density 0.920 g/cc with a poly(butene-1) of melt index 2.0 g/10 min. and a density of 0.908 g/cc and a high density polyethylene grafted with x-methyl bicyclo(2.2.1)hept-5-ene-2,3-dicarboxylic acid anhydride (XMNA) similar to that used in Example 1 to obtain blends having the weight percent compositions listed.

These blends were then heat-sealed to ethylene-vinyl alcohol copolymer at 430°F (221°C) for 1 sec. The adhesions obtained are listed in the last column below:

	Example	LLDPE	Poly(butene-1)	Graft Copolymer	Adhesion lbin (kg/cm)	
	6	90	0	10	2.3 (0.41)	
5	7	80	10	10	>8.8*(1.58)	5
	8	70	20	10	>8.5*(1.53)	
	9	60	30	10	>9.9*(1.78)	
	10	50	40	10	>7.1 (1.28)	
	11	45	45	10	>7.6 (1.37)	
10	12	30	60	10	6.6 (1.19)	10
	13	80	0	20	6.0 (1.08)	
	14	70	10	20	>10.0*(1.8)	
	15	60	20	20	>10.0*(1.8)	
	16	20	60	20	3.8 (0.68)	
15	17	85	5	10	>5.4 (0.97)	15
	18	75	5	20	>5.1 (0.92)	
	19	88	2	10	2.9 (0.52)	
	20	89	1	10	3.9 (0.70)	
	21	86.5	3.5	10	4.9 (0.88)	
20	22	89.5	0.5	10	3.7 (0.67)	20

* indicates could not peel apart

Examples 23-25

25 An electrically heated C.W. Brabender mixing unit was used to blend a linear low density polyethylene resin (LLDPE) of melt index 1 g/10 min. and density 0.924 g/cc with a poly(butene-1) resin (PB) of melt index 2.0 g/10 min. and density 0.908 g/cc and a high density polyethylene grafted with x-methyl bicyclo (2.2.1)hept-5-ene-2,3-dicarboxylic acid anhydride (XMNA), in the following percentage ratios.

30 The adhesions were carried out in a heat-sealer at 430°F (221°C) for 1 sec. The adhesion values in lb/in (kg/cm) obtained to aluminium film (A1), ethylene-vinyl alcohol copolymer film (EVOH), and nylon 6 (N-6) are given below: 30

Example	Percentage in Blend			Adhesion to Substrate			
	LLDPE	PB	Graft Copolymer	A1	EVOH	N-6	
35							35
	23	80	10	10	4.8 (0.86)	>5.9 (1.06)	>5.0* (0.9)
	24	90	0	10	3.7 (0.67)	0.8 (0.14)	3.6 (0.65)
40	25	70	20	10	>10.0*(1.8)	>6.8 (1.22)	>4.3* (0.77)

* Indicates the samples could not be peeled apart

45 **Examples 26-27** 45

Instead of the linear low density polyethylene used in Examples 23-25, a low density polyethylene resin (LDPE) of melt index 1.8 g/10 min. and density 0.922 g/cc was used to make the blends of Examples 26 and 27 respectively.

50 The adhesion values lbs/in (kg/cm), obtained after heat-sealing to EVOH and Nylon 6 are given below: 50

Example	Percentage in Blend			Adhesion to Substrate		
	LDPE	PB	Graft Copolymer	EVOH	Nylon 6	
55						55
	26	80	10	10	>6.5 (1.17)	3.8 (0.68)
	27	70	20	10	>5.7 (1.03)	>4.2 (0.76)

60 **Examples 28-29** 60

Instead of the linear low density polyethylene used in Examples 23-25, a low density polyethylene (LDPE) of melt index 2.5 g/10 min. and density 0.919 g/cc was used in formulating the blends of Examples 28 and 29. A linear low density polyethylene grafted with x-methyl bicyclo(2.2.1)hept-5-ene-2,3-dicarboxylic acid anhydride, with melt index of 5.1 g/10 min. was used instead of the grafted HDPE.

The adhesions obtained to ethylene-vinyl alcohol copolymer film (EVOH) and to nylon 6 film are given below in lbs/in (kg/cm):

5	Example	Percentage in Blend			Adhesion to Substrate		5
		LDPE	PB	Graft Copolymer	EVOH	Nylon 6	
	28	90	0	10	2.2 (0.40)	3.1 (0.56)	
10	29	80	10	10	>7.9*(1.42)	>4.0 (0.72)	10

* Indicates could not separate

Examples 30-31

15 The low density polyethylene used in Examples 28 and 29 was substituted by another low density polyethylene of broad molecular weight distribution with a melt index of 5.5 g/10 min. and a density of 0.923 g/cc. The graft copolymer used in these cases was that used in Example 1.

Adhesions obtained to ethylene-vinyl alcohol copolymer film (EVOH) and to a copolyester film are given below in lbs/in (kg/cm):

20	Example	Percentage in Blend			Adhesion to Substrate		20
		LDPE	PB	Graft Copolymer	EVOH	Copolyester*	
	30	90	0	10	3.9 (0.70)	3.2 (0.58)	
25	31	80	10	10	>5.7 (1.03)	>5.1 (0.92)	25

30 * The heat sealer used was set at 500°F (260°C) and 5 seconds. The copolyester was a glycol-modified polyethylene terephthalate (PETG)

Example 32

35 The blend used in Example 29 was tested for adhesion to the same copolyester tested in Examples 30 and 31. The adhesion obtained was greater than 7.9 lbs/in (1.42 kg/cm).

Example 33

40 The blend used in Example 7 was tested for adhesion to a commercial rubber-modified acrylonitrile-methacrylate copolymer film with the heat sealer set at 350°F (177°C) for 1 sec. The adhesion obtained was greater than 8.1 lbs/in (1.46 kg/cm).

Example 34

45 A blend of 80% low density polyethylene used in Example 28, 10% poly(butene-1) copolymer used in Example 3, and 10% of the high density polyethylene graft copolymer used in Example 1 gave an adhesion greater than 4.0 lbs/in (0.72 kg/cm) when heat-sealed to a polyethylene terephthalate film (PET) with the heat sealer set at 500°F (260°C) and 5 sec.

Example 35

50 A blend of 80% ethylene-vinyl acetate copolymer with melt index of 12.0 g/10 min. and 12% vinyl acetate content, 10% of the poly(butene-1) used in Example 3, and 10% of the linear low density polyethylene graft copolymer used in Example 28 gave an adhesion greater than 4.6 lb/in (0.83 kg/cm) when heat-sealed at 350°F (177°C) and 1 sec. to aluminium foil.

Examples 36-37

55 Blends of an ethylene-vinyl acetate copolymer (EVA) of melt index 3.0 g/10 min. and 9% vinyl acetate content with the poly(butene-1) used in Example 3, and 10% of the linear low density polyethylene graft copolymer used in Example 28 were prepared with the following compositions.

These blends were tested for adhesion to aluminium (A1) foil with the Sentinel heat sealer set at 250°F (121°C) and 1 sec. The adhesion values obtained are shown below in lbs/in (kg/cm):

Example		Percentage in Blend			Adhesion to Substrate	
		EVA	Graft	PB	Al	
5	36	90	10	0	0.8 (0.14)	5
	37	80	10	10	3.0 (0.54)	

Examples 38-39

Blends 38 and 39 were prepared similar to blends in Examples 36 and 37, respectively, except the ethylene-vinyl acetate copolymer (EVA) was changed to the one used in Example 35. These blends were then tested for adhesion to ethylene-vinyl alcohol copolymer film (EVOH) with the Sentinel heat sealer set at 430°F (221°C) and 1 sec. The results of the adhesion are shown below in lbs/in (kg/cm):

Example		Percentage in Blend			Adhesion to Substrate	
		EVA	PB	Graft Copolymer	EVOH	
20	38	90	0	10	3.9 (0.70)	20
	39	80	10	10	>5.1 (0.92)	

Examples 40-41

Blends were prepared with the following compositions containing the linear low density polyethylene used in Example 6, the poly(butene-1) used in Example 3, and a high density polyethylene graft copolymer grafted with maleic anhydride.

The adhesions obtained to ethylene-vinyl alcohol copolymer (EVOH) when heat-sealed at 430°F (221°C) for 1 sec. are shown below in lbs/in (kg/cm):

Example		Percentage in Blend			Adhesion to Substrate	
		LLDPE	Graft Copolymer	PB	EVOH	
35	40	90	10	0	3.1 (0.56)	35
	41	80	10	10	>7.5 (1.35)	

Examples 42-43

Blends were prepared with the following compositions containing the linear low density polyethylene used in Example 6, the high density graft copolymer used in Example 1, and poly(4-methyl pentene-1) (P4MP). These blends were tested for adhesion to aluminium foil, nylon 6 film, and ethylene-vinyl alcohol copolymer (EVOH) film with the heat sealer set at 430°F (221°C) and 1 sec., respectively. The adhesions shown below are in lbs/in (kg/cm):

45	Example	Percentage in Blend				Adhesion to Substrate		45
		LLDPE	Graft Copolymer	P4MP	Nylon	A1	EVOH	
50	6	90	10	0	2.9(0.52)	3.0(0.54)	2.3(0.41)	50
	42	80	10	10	2.3(0.41)	>3.0(0.54)	2.3(0.41)	
	43	65	10	25	>5.4(0.97)	>7.4(1.33)	>4.0(0.72)	

Examples 44-45

The blends used in Examples 31 and 29 were cast-coextruded with ethyl-vinyl alcohol copolymer (EVOH). The co-extruded cast films obtained had a total thickness of about 3 mils (0.076mm). The layer of adhesive blend had a thickness of 1.5 mil (0.038mm). The adhesions obtained were greater than 1.8 lb/in (0.32 kg/cm) with blend No. 31 and 2.0 lb/in (0.36 kg/cm) with blend No. 29. The film elongated during the T-peel test in each case.

Glossary of Terms

Al	- aluminium foil	
EVA	- ethylene vinyl acetate copolymer	
EVOH	- ethylene-vinyl alcohol copolymer	
HDPE	- high density polyethylene	

	LDPE	- low density polyethylene	
	N-6	- Nylon-6 film	
	LLDPE	- linear low density polyethylene	
	PE	- polyethylene	
5	PB	- poly(butene-1)	5
	PETG	- polyethylene terephthalate glycol-modified	
	PP	- polypropylene	
	PVA	- polyvinyl alcohol	
	P4MP	- poly(4-methyl pentene-1)	
10	PET	- polyethylene terephthalate	10
	XMNA	- x-methylbicyclo(2.2.1)hept-5-ene-2,3-dicarboxylic acid anhydride	

CLAIMS

- 15 1. An adhesive blend which comprises, by weight: 15
 - (a) from 0.1 to 40 parts of a graft polymer of from 70 to 99.999% of a polyethylene backbone grafted with from 30 to 0.001% of at least one grafting monomer which is a polymerizable ethylenically unsaturated carboxylic acid or derivative thereof, for a total of 100%,
 - (b) from 0.1 to 99 parts of LDPE, an ethylene-unsaturated ester copolymer, or LLDPE, or a mixture of two or more thereof, and 20
 - (c) from 0.1 to 99 parts of at least one homopolymer or copolymer of an α -olefin having 4 to 15 carbon atoms, for a total of 100 parts. 20
2. An adhesive blend according to claim 1, in which the grafting monomer acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, mesaconic acid, maleic anhydride, 4-methyl 25 cyclohex-4-ene-1,2-dicarboxylic acid anhydride, bicyclo (2.2.2)oct-5-ene-2,3-dicarboxylic acid anhydride, 1,2,3,4,5,8,9,10-octahydronaphthalene-2,3-dicarboxylic acid anhydride, 2-oxa-1,3-diketospiro(4.4)non-7-ene, bicyclo (2.2.1)hept-5-ene-2,3-dicarboxylic acid anhydride, maleopimaric acid, tetrahydrophthalic anhydride, norborn-5-ene-2,3-dicarboxylic acid anhydride, Nadic anhydride, methyl Nadic anhydride, Himic anhydride, methyl Himic anhydride, or x-methyl bicyclo(2.2.1)hept-5-ene-2,3-dicarboxylic acid anhydride. 25
- 30 3. An adhesive blend according to claim 1 or 2, in which the unsaturated ester present in the ethylene-unsaturated ester copolymer of (b) is vinyl acetate, methyl or ethyl acrylate, or methyl or ethyl methacrylate. 30
4. An adhesive blend according to claim 1 or 2, in which the LLDPE of (b) is a copolymer of ethylene and an unsaturated hydrocarbon.
- 35 5. An adhesive blend according to claim 4, in which the unsaturated hydrocarbon is propylene, butene-1, 4-methyl-pentene-1, hexene-1, or octene-1. 35
6. An adhesive blend according to any of claims 1 to 5, in which the α -olefin of component (c) is butene-1, 4-methyl-pentene-1, hexene-1, octene-1 or pentene-1.
7. A composite structure comprising a substrate and, adhered thereto, an adhesive blend according to any of claims 1 to 6. 40
8. A composite structure according to claim 7, in which the substrate is formed of a polyolefin, a polar polymer, metal, glass, paper, wood, leather or regenerated cellulose.
9. A composite structure according to claim 7 or 8, in which the substrate is formed of an ethylene homopolymer or copolymer, nylon, polyester, rubber-modified acrylonitrile-methacrylate copolymer, or aluminium. 45
10. A composite structure comprising two or more substrates with adjacent pairs of substrates adhered together by an interposed layer of an adhesive blend according to any of claims 1 to 6.
11. A composite structure according to claim 10, in which one substrate is a polar substrate and the adjacent substrate is formed of nylon, ethylene-vinyl alcohol copolymer, aluminium, a polyester or copolyester, an ethylene homo- or co-polymer, or a propylene homo- or co-polymer. 50
12. A composite structure according to claim 11, in which the ethylene copolymer is ethylene-vinyl acetate copolymer.
13. A composite structure according to claim 11 or 12, in which the polar substrate is formed of nylon, polyvinyl alcohol, ethylene-vinyl alcohol copolymer, polyester, aluminium, steel, copper, glass, wood, or polyurethane. 55
14. A composite structure according to claim 10, in which a first substrate is formed of polypropylene or polyethylene, a second substrate of a polar polymer or metal, and a third substrate of an ethylene homo- or co-polymer or polypropylene.
15. A composite structure according to claim 14, in which the second substrate is formed of nylon, ethylene-vinyl alcohol copolymer, or aluminium. 60
16. A composite structure according to claim 14 or 15, in which the third substrate is formed of ethylene-vinyl acetate copolymer.

17. An adhesive blend substantially as herein described in any of Examples 1 to 5, 7 to 12, 14 to 23, 25 to 27, 29, 31 to 35, 37, 39, and 41 to 45.

18. A composite structure substantially as herein described in any of Examples 1 to 5, 7 to 12, 14 to 23, 25 to 27, 29, 31 to 35, 37, 39, and 41 to 45.

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